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## **INFLUENCE OF THERMALLY TREATED PHOSPHOGYPSUM ON THE PROPERTIES OF PORTLAND SLAG CEMENT**

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### **Abstract**

In this study, thermal treatment of phosphogypsum(PG) at different temperatures 200,400,600 and 800 °C were attempted to purify PG and improve its quality to make it fit for the manufacture of Portland slag cement (PSC). PG is a waste of phosphoric acid manufacturing by dehydrate process in Egypt. It is a fine powder with high calcium sulphate content. This waste causes various environmental problems when discharged directly to the environment. The thermally treated PG was found to have lesser amount of impurities of phosphates, fluorides and organic matter than the impure material. In this investigation, preparation of Portland slag cement (PSC) in laboratory was carried out by mixing Portland cement clinker (PCC) and Blast-furnace slag (BFS) with thermally treated PG at different temperatures instead of raw gypsum (RG). The characteristics of prepared mortars were investigated by determination of compressive strength, bulk density and total porosity. The hydration kinetics of cement mortars was evaluated by determination free lime and chemically combined water contents. IR spectroscopic analysis was used to investigate the change in structure of mortars after curing... The change in morphology and microstructure of some hardened pastes were investigated by scanning electron microscopy (SEM) tests. The results show that, Portland slag cement produced using 6% thermally treated PG at 800°C improves its hydraulic properties.

**Keyword:** Thermal treatment, Phosphogypsum, Clinker, Blast furnace slag, Slag cement.

### **Introduction:**

Phosphogypsum (PG) is a kind of gypsum that occurs as a by-product and is obtained from phosphate rock during the production of phosphoric acid. PG can be used as a blending component in Portland blended cement in order to conserve energy, save environment, improve quality and reduce the cost production of cements [1,2]. PG contains some impurities such as P<sub>2</sub>O<sub>5</sub> and fluorides so in order to use it as cement retarded instead of raw gypsum (RG), purification, drying and calcinations processes must be applied [3-5]. The usage of the PG as a retarder replacement of RG provides both economical and ecological profits. There are several researchers on the usage of phosphor-, citro, and borogypsum as a retarder in the manufacturing of cement [6-12]. Smadi et al [13] calcined PG at 170,600,750,850 and 950 °C after washed and not washed with water. The amount

of  $P_2O_5$  in the calcined and wash samples was 0.41% after the calcinations at 170°C; however, it decreased to 0.32% after the calcinations at 950°C, and fluoride amount decreased from 0.89% to 0.27% at the same temperatures. In the sample that was not washed with water, no significant decrease in  $P_2O_5$  at the same calcinations temperatures was observed, but the fluoride decreased from 2.12% to 0.16% with increasing the calcinations temperatures from 170 to 950 °C. Also, the setting times increased on using PG for calcined and uncalcined samples. The effect of different mineralizers on the decrease of burning temperature of Portland clinker was the object of many researches. Fluorosilicates improve the chemical activity of clinker minerals and accelerate the reactions of clinkerization at low temperatures (1300-1350°C) [14]. Fluorides according to different authors [15], have also favorable action on the formation of clinker minerals by decreasing the thermal energy consumption. PG when heated at elevated temperature, produced anhydrite and the impurities become inert. The formation of anhydrite cement was examined by microscopy and X-ray diffraction method. Data showed that a stable anhydrite can be produced by heating PG at 1000°C [16] . The substitution of Portland cement with 5% calcined PG at 800°C in presence of 5% silica fume improves the hydraulic properties of cement due to the presence of calcined PG enhances the formation of ettringite [17]. Blast furnace slag is the most important and useful material for cement industry and considerable amount of search work has been done on this material[18-21]. The effect of unprocessed PG and fluorogypsum added independently and in combination with natural gypsum on various properties of Portland and Portland slag cement was investigated [22]. The results showed that the adverse effect of  $P_2O_5$  and fluorides impurities in PG and those of fluorogypsum could be offset by blending natural gypsum. An increase in compressive strength and decrease in setting time of cement was observed on using blended gypsum. Also, the properties of Portland cement and Portland slag cement with blended gypsum conformed to the requirement of cement produced with natural gypsum. The aim of the present investigation is to study the effect of using thermally treated PG instead of RG for the manufacturing of Portland slag cement...

### **Experimental:**

#### *Materials:*

PG, which may be added to PCC, is obtained as by-product during the production of phosphoric acid from phosphate rock in Abu-Zabal fertilizer and chemical Industries Company (near Cairo, Egypt). PCC, RG and BFS, which were used in the present experimental study, have been brought from Assiut Cement

Company (Assiut, Egypt). The PCC phases and their percentages amounts as calculated from Bogue analysis method are as follows: C<sub>3</sub>S 58.24%, C<sub>2</sub>S 16.52%, C<sub>3</sub>A 10.42% and C<sub>4</sub>AF 11.10%. The chemical composition of starting materials PCC, PG, RG and BFS are given in Table (1).

**Table(1): Chemical composition of starting materials (mass %):**

Constituents	PCC	PG	RG	BFS
SiO <sub>2</sub>	23.20	8.77	3.15	
Al <sub>2</sub> O <sub>3</sub>	5.88	0.29	0.13	
Fe <sub>2</sub> O <sub>3</sub>	3.45	0.35	0.23	
CaO	63.37	32.13	35.09	
MgO	2.21	0.09	0.05	
SO <sub>3</sub>	0.59	34.52	42.12	
P <sub>2</sub> O <sub>5</sub>	---	1.72	---	
F	---	0.80	---	
LL	0.75	21.05	19.00	

The mix compositions of the prepared PSC with mix numbers are given in Table (2).

**Table(2): Mix compositions and mixes No. of the prepared PSC, mass%**

Mix Composition	Mix No.
54% PCC + 40% BFS + 6% uncalcined PG	M1
54% PCC + 40% BFS + 6% calcined PG at 200°C	M2
54% PCC + 40% BFS + 6% calcined PG at 400°C	M3
54% PCC + 40% BFS + 6% calcined PG at 600°C	M4
54% PCC + 40% BFS + 6% calcined PG at 800°C	M5
54% PCC + 40% BFS + 6% RG	M6

*Methods:*

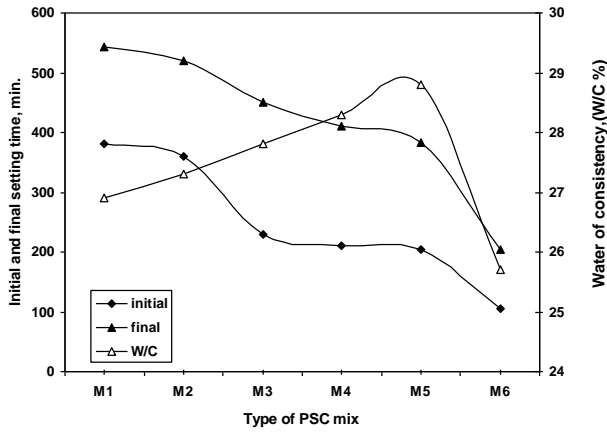
The thermal treatment of PG has been done by heating PG for 2 hours in muffle furnace for the required temperatures in this investigation 200,400,600 and 800°C with heating rate 10°C/minute. After every calcined temperature, PG was cooled, crushed and ground in agate mortar machine, then sieved completely through 90 µm sieve. Also, RG, PCC and BFS were separately crushed and ground in the agate mortar machine, then sieved through 90 µm sieve. The ingredients of each mix were blended in a porcelain ball mill for two hours using a mechanical roller to insure

complete homogeneity. The required water of standard consistency and setting time for each mix were determined according to ASTM specifications [23, 24]. The mortars were prepared by adding water to every mix according its water of consistency value, and then molded in one inch cubic moulds. The specimens were cured in a humidity chamber at  $23 \pm 1^\circ\text{C}$  for 24 hours, then demolded and immersed in tap water until tested. After the predetermined curing time 3,7,28 and 90 days, groups of three specimens were used to determine the residual compressive strength according to ASTM specification [25]. Bulk density and total porosity were determined after any time of hydration as described elsewhere [26]. The hydration of cement pastes were stopped by employing alcohol-ether method [27]. The samples were dried at  $105^\circ\text{C}$  for one hour and then collected in polyethylene bags; sealed and stored in desiccators for analysis. The degree of hydration was followed by determination of free lime [28] and chemically-combined water content [29]. The hydration products were analyzed by FTIR spectrophotometric technique using a Perkin Elmer System 2000 FTIR spectrometer. The morphology and microstructure of some dry samples were investigated using scanning electron microscope (JEOL JSM-840 SEM).

### **Results and discussion:**

#### *Water of consistency and setting time:*

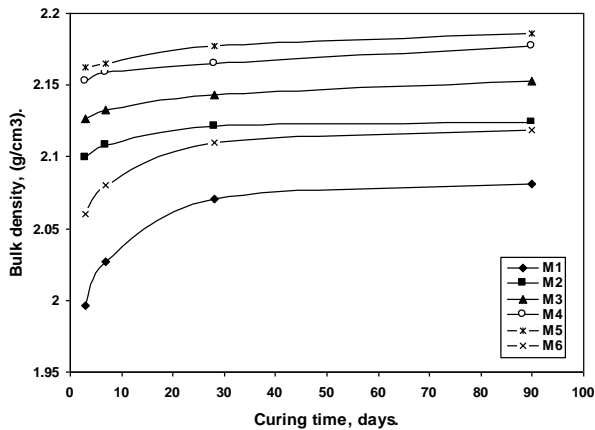
Figure 1 shows the required water of standard consistency and setting times of the prepared slag cement. The results show that, the water of consistency increased as the firing temperature of PG increased. The paste containing PG fired at  $800^\circ\text{C}$  possess the highest water of consistency value. Also, initial and final setting time of PSC pastes decreased as the firing temperature of PG increases and paste containing fired PG at  $800^\circ\text{C}$  possess lower initial and final setting time. The reasons of all these results are attributed to thermal treatment of PG, which decreases the pronounced effect of, water soluble  $\text{P}_2\text{O}_5$  and fluorides ( $\text{NaF}$  and  $\text{Na}_2\text{SiF}_6$ ) present in PG. This forms protective coatings as the inactive substances ( $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaHPO}_4$ ,  $\text{CaF}_2$ ) which produce by the impurities on the surface of cement grains during the gauging of cement with water and thus suppression of the hydration of cement temporarily [30]. It is clear that, PSC pastes made from RG possess lower water of consistency and lower initial and final setting time. PSC pastes made from unfired PG possess higher water of consistency and higher initial and final setting time.



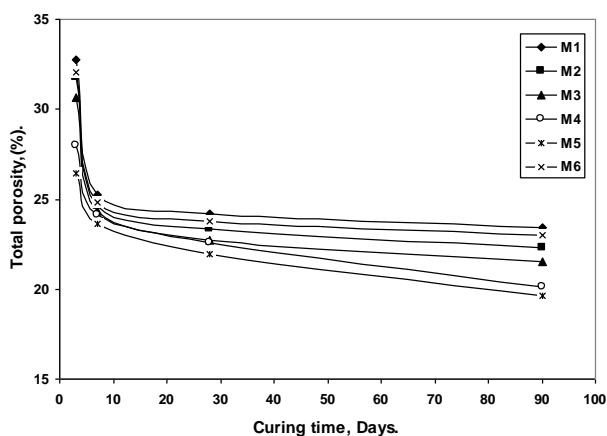
**Fig.(1):** Water of consistency and setting times of different PSC pastes containing calcined PG at different temperatures.

*Bulk density and total porosity:*

The values of bulk density and total porosity of the hydrated slag cement pastes prepared using calcined PG at different temperatures are graphically represented as a function of curing time in Figures 2 and 3, respectively. The results show continuous increase in the bulk density values and decrease of total porosity values with longer hydration time for all samples as a result of cement hydration progress up to 90 days. This mainly attributed to the formation and coagulation of hydration products, which fill up some of the open pores, thus increasing in bulk density and decreasing in total porosity values. PSC specimens containing calcined PG at 800°C possess higher bulk density and lower porosity values at all age of hydration.



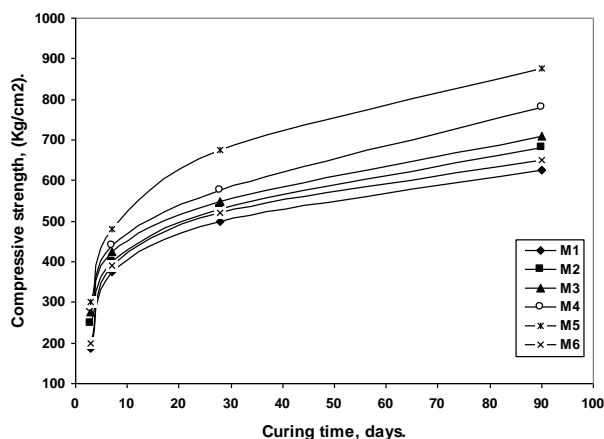
**Fig(2):** Bulk density of PSC hardened pastes containing calcined PG at different temperatures as a function of curing



**Fig(3): Total porosity of PSC hardened pastes containing calcined PG at different temperatures as a function of curing time.**

*Compressive strength:*

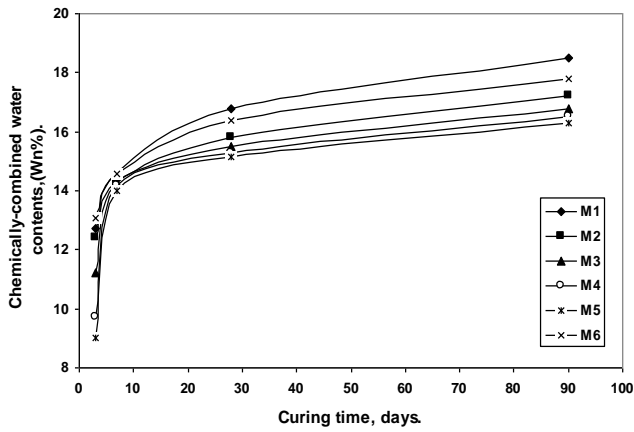
The effect of thermally treated PG on the compressive strength of PSC specimens is illustrated in Fig.4. It can be seen that the strength increases with the increasing curing period. Maximum attainment of strength was notice in case of PSC specimens containing calcined PG at 800°C. This is attributed to the thermal treatment of PG which decreases the  $P_2O_5$  and fluorides contents, so decrease their retardation effect on the hydration products. These products accumulate in water filled pores to form a more compact body. PSC specimens containing calcined PG at 800°C possess higher compressive strength values at all curing periods. It is clear that, the bulk density and total porosity values are in great agreement with compressive strength values.



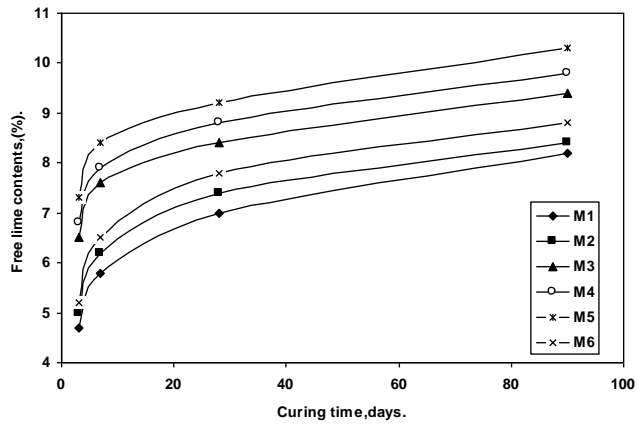
**Fig.(4): Compressive of PSC hardened pastes containing calcined PG at different temperatures as a function of curing time.**

*Degree of hydration:*

The degree of hydration is measured from the chemically-combined water and free lime contents. Figures 5 and 6 show the variation of chemically combined water and free lime contents of PSC pastes, respectively.. The chemically combined water contents increase gradually with increasing curing time for all hardened cement pastes (Fig.5). This is due to the progress of hydration with increasing curing time and the accumulation of hydration products. Also, the free lime contents increase with increasing curing time (Fig.6) due to the continuous hydration of the main cement clinker phases  $\beta$ -C<sub>2</sub>S and C<sub>3</sub>S; liberating free lime.



**Fig.(5): Chemically- combined water contents of PSC pastes containing calcined PG at different temperatures as a function of curing time.**

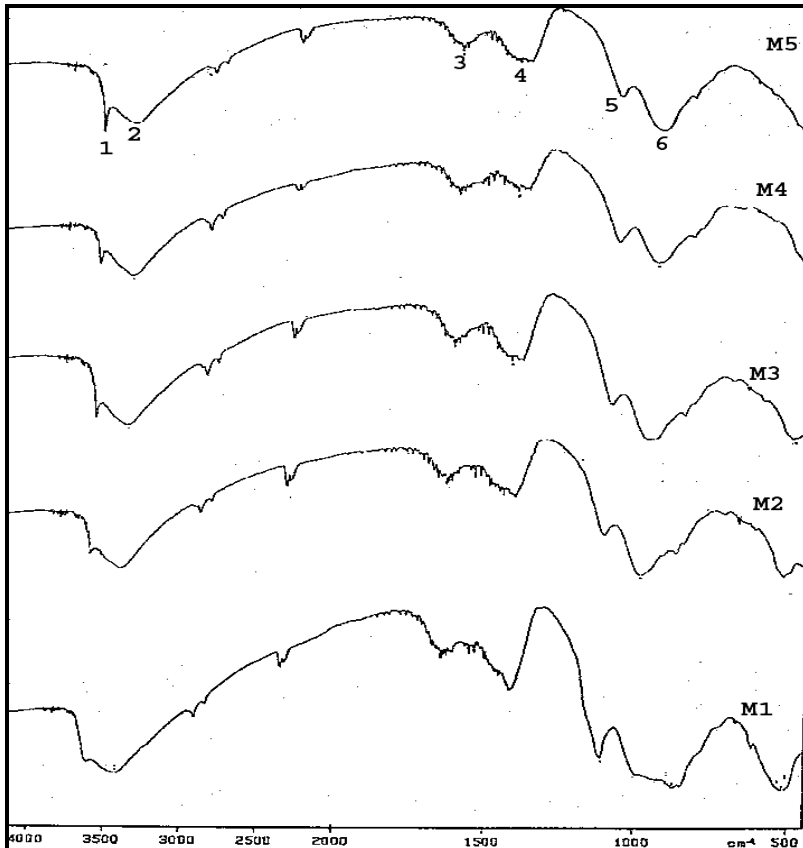


**Fig.(6): Free lime contents of PSC pastes containing calcined PG at different temperatures as a function of curing time.**



*FTIR analysis:*

The FTIR patterns of hydration products of different PSC pastes (M1-M5) after 90 days curing are shown in Fig. 7. It is clear that, the band at  $3644\text{ cm}^{-1}$  which is due to the stretch vibration of OH group of protlandite (CH)[31] increases with increasing firing temperature of PG due to progress of hydration.. The peak at  $3431$  is due to water [32]. The band at  $1458\text{ cm}^{-1}$  is attributed to presence of calcite, possibly formed due to aeration of the pastes [33]. A singlet band due to the vibration of sulphate( gypsum in anhydrous cement) located at  $1120\text{ cm}^{-1}$  [34]. The intensity of the band at  $987\text{ cm}^{-1}$  which is due to Si-O stretching vibration of C-S-H [31] increases with increasing firing temperature of PG indicating increasing of formation of CSH in the order from M1 to M5, i.e. M5 has higher hydraulic properties.



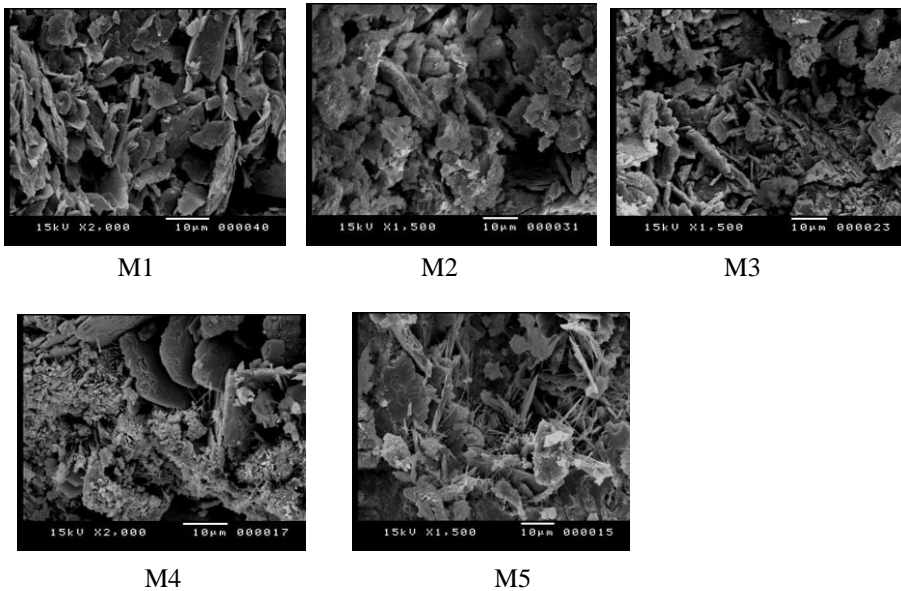
Wavenumber  $\text{cm}^{-1}$

(1=  $3644\text{cm}^{-1}$ , 2=  $3431\text{ cm}^{-1}$ , 3=  $1654\text{cm}^{-1}$ , 4=  $1458\text{cm}^{-1}$  and 5=  $1120\text{cm}^{-1}$  and 6=  $987\text{cm}^{-1}$ )

Fig.(7): Infrared spectra of PSC pastes (M1-M5) after 90 days curing

*Morphology and microstructure:*

The effect of thermally treated PG at different temperatures on the morphology and microstructure of prepared PSC pastes was analyzed under scanning electron microscope. The micrographs of different PSC pastes M1, M2, M3, M4 and M5 after 90 days curing are shown in Fig.(8). The micrograph M1 indicates that it had a flocculent and porous structure. In this paste the wider pores are available for crystallization of the formed hydrates. So, this paste has lower strength due to higher porosity. The micrograph M2 indicates formation of microcrystalline CSH and opening pore system. The micrograph of M3 indicates that a large amount of CSH gel formed. This has not only formed a dense surface coverage on the cement pastes, but is also developed in the pores. It shows also, the presence of ettringite and  $\text{Ca}(\text{OH})_2$ . The micrograph M4 indicates formation of fibrous and crystalline CSH. The micrograph M5 is composed of dense structure of platelet-like hydrates of CSH and crystalline hydrates having close texture structure with interlocking arrangements. The micrograph also, shows longer rod like particles of CSH, but  $\text{Ca}(\text{OH})_2$  did not survive in nature-hydrated pastes. Therefore, this paste has a higher degree of hydration and higher strength value. The results of SEM are in harmony with the compressive strength values.



**Fig.(8): SEM micrographs of studied PSC pastes after 90 days water curing.**

**Conclusion:**

From this study we can concluded that:

- 1- Using thermally treated phosphogypsum at 400,600 and 800°C instead of raw gypsum improves the hydraulic properties of Portland slag cement.
- 2- The highest hydraulic properties of Portland slag cement occurs by using thermally treated phosphogypsum at 800°C.

*Abbreviations in cement chemistry*:: C= CaO, H=H<sub>2</sub>O, S=SiO<sub>2</sub>, A=Al<sub>2</sub>O<sub>3</sub>

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## الملخص العربي

تأثير الجبس الفوسفاتي المعالج حرارياً على خواص الأسمنت البورتلاندى الحديدى

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يعتبر الجبس الفوسفاتى المتخلف من مصانع الأسمدة فى مصر من أهم المشاكل التى تهدد البيئة وذلك لأحتوائه على مركبات عضوية وفلوريدات ضارة بالبيئة. وينتج الجبس الفوسفاتى نتيجة لعملية تحضير حمض الفوسفوريك اللازم لعملية تصنيع الأسمدة الفوسفاتية وذلك بتفاعل حمض الكبريتيك مع صخر الفوسفات ونتيجة لهذه العملية فإن كل طن ناتج من حمض الفوسفوريك يقابله 5 طن من الجبس الفوسفاتى وهى كمية كبيرة تؤثر تأثير ضار على البيئة. والجبس الفوسفاتى غنى بكبريتات الكالسيوم  $CaSO_4$  ولذلك فمن الممكن استخدامه فى صناعة الأسمنت بعد معالجته حرارياً للتخلص من المركبات العضوية وتقليل نسبة الفلوريدات.

فى هذا البحث تم دراسة تأثير استخدام الجبس الفوسفاتى (PG) المحروق عند درجات حرارة 200 و 400 و 600 و 800 درجة مئوية بدلاً من خام الجبس (RG) على الخواص الفيزيوكيميائية والميكانيكية وكذلك كيناتيكية التآدرت للأسمنت البورتلاندى الحديدى الذى تم تحضيره داخل المعمل. وقد تم دراسة الخواص الفيزيوكيميائية بقياس نسبة الماء المتحد والجير الحر وقوة الأنضغاط والكثافة الحجمية والمسامية لعجائن الأسمنت البورتلاندى الحديدى بعد غمرها فى الماء فى الأزمنة 3 و 7 و 28 و 90 يوم. وكذلك تمت دراسة التغير فى الأطوار عند زمن 90 يوم باستخدام القياسات الطيفية للأشعة تحت الحمراء (IR spectroscopy). وتمت دراسة التغير فى التركيب الدقيق لبعض العينات باستخدام الماسح الألكترونى (Scanning electron microscope).

وقد وجد أن نسبة الماء المتحد والجير الحر والكثافة وقوة الأجهاد تزداد بزيادة زمن الغمر حتى 90 يوم بينما تقل المسامية وذلك لكل العينات المحروقة وعند كل درجات حرارة حرق جبس الفوسفات. وقد أوضحت نتائج هذه القياسات والقياسات الأخرى باستخدام الأشعة تحت الحمراء والماسح الألكترونى أن أعلى خواص هيدروليكية للأسمنت البورتلاندى الحديدى تتحقق باستخدام جبس الفوسفات المحروق عند 800 درجة مئوية ولذلك فإنه يمكن استخدامه كبديل للجبس الخام فى صناعة الأسمنت البورتلاندى الحديدى.